

Gas Production from Water on Oxides and Salts

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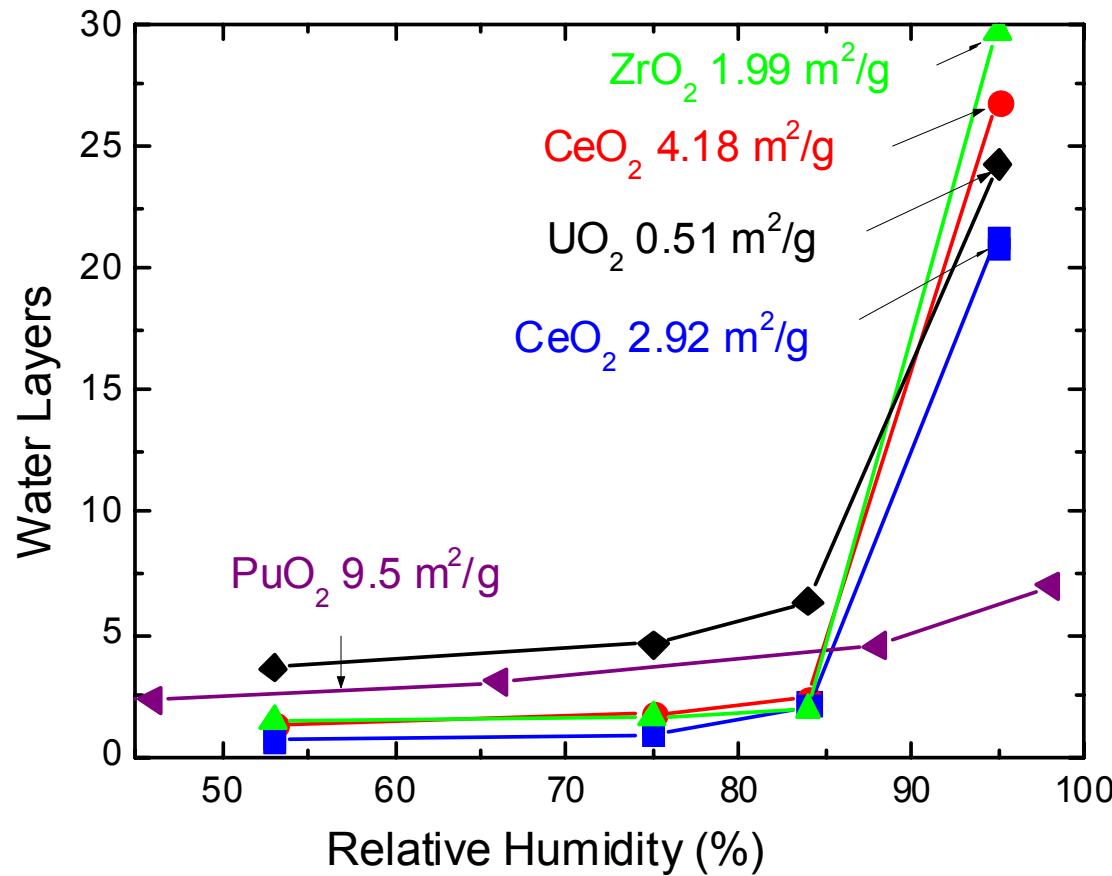
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Water Layer Dependence on Relative Humidity

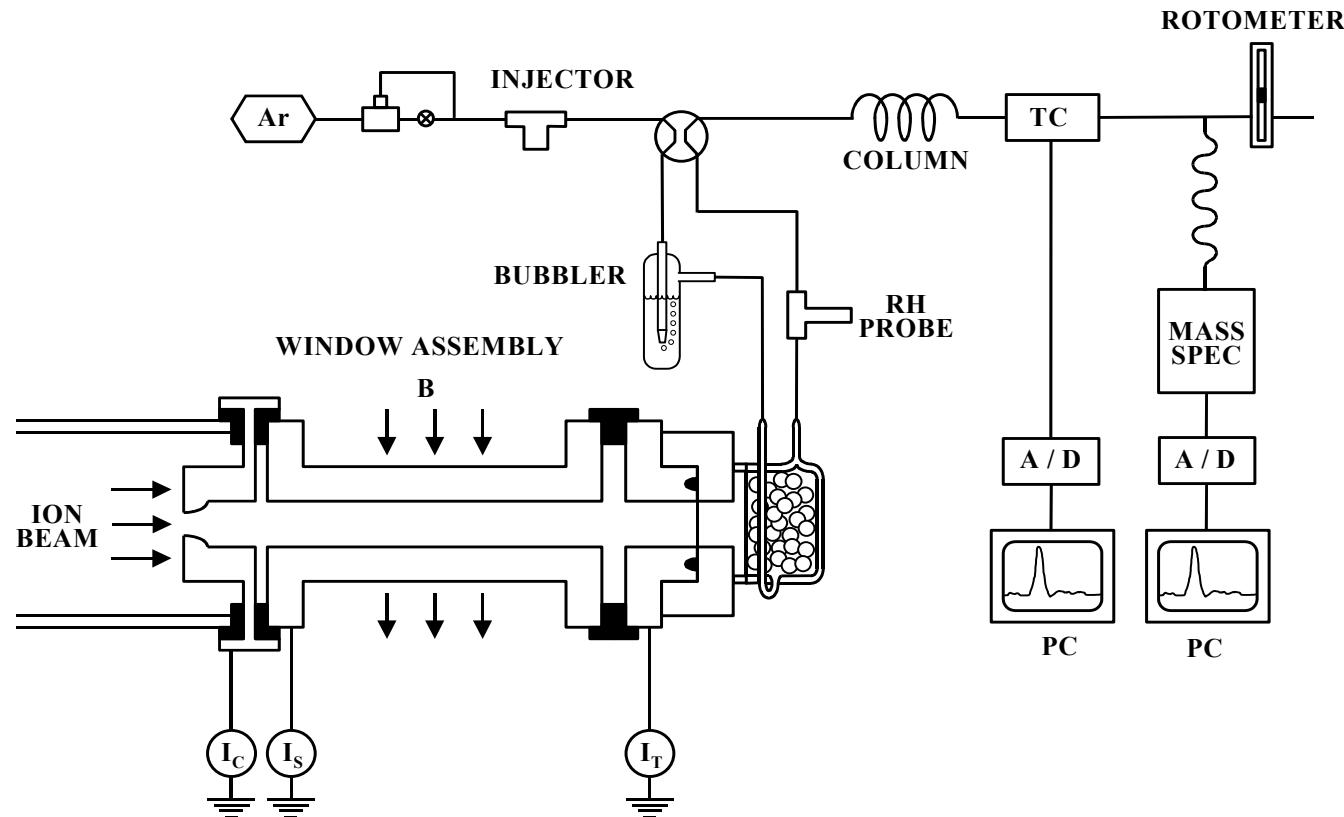
PuO_2 : A. Benhamou and J. P. Beraud *Analisis*, **8**, 376-380 (1980).

Assume 0.22 mg $\text{H}_2\text{O}/\text{m}^2$



Few (1-4) water layers until high relative humidity.

Heavy Ion Radiolysis Assembly

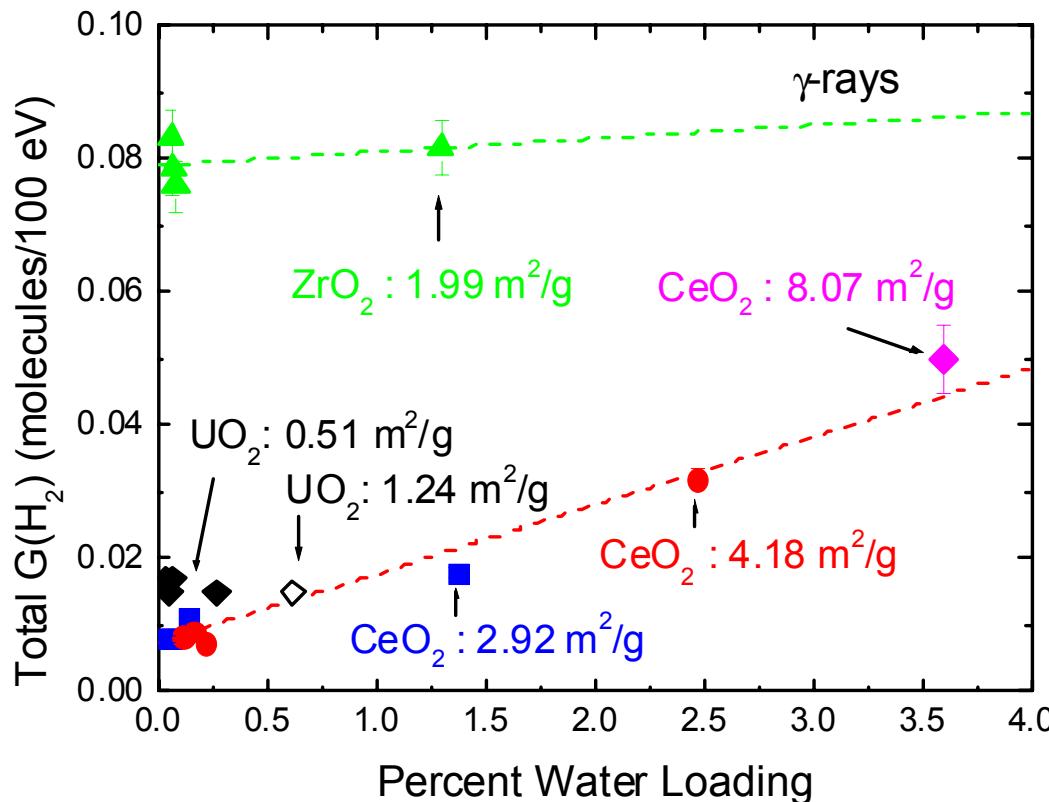


Inline gas chromatograph for radiolysis and gas analysis.

Total G-values for H₂ Production in γ -Radiolysis

J. A. LaVerne and L. Tandon *J. Phys. Chem. B.* **2002**, 106, 380.

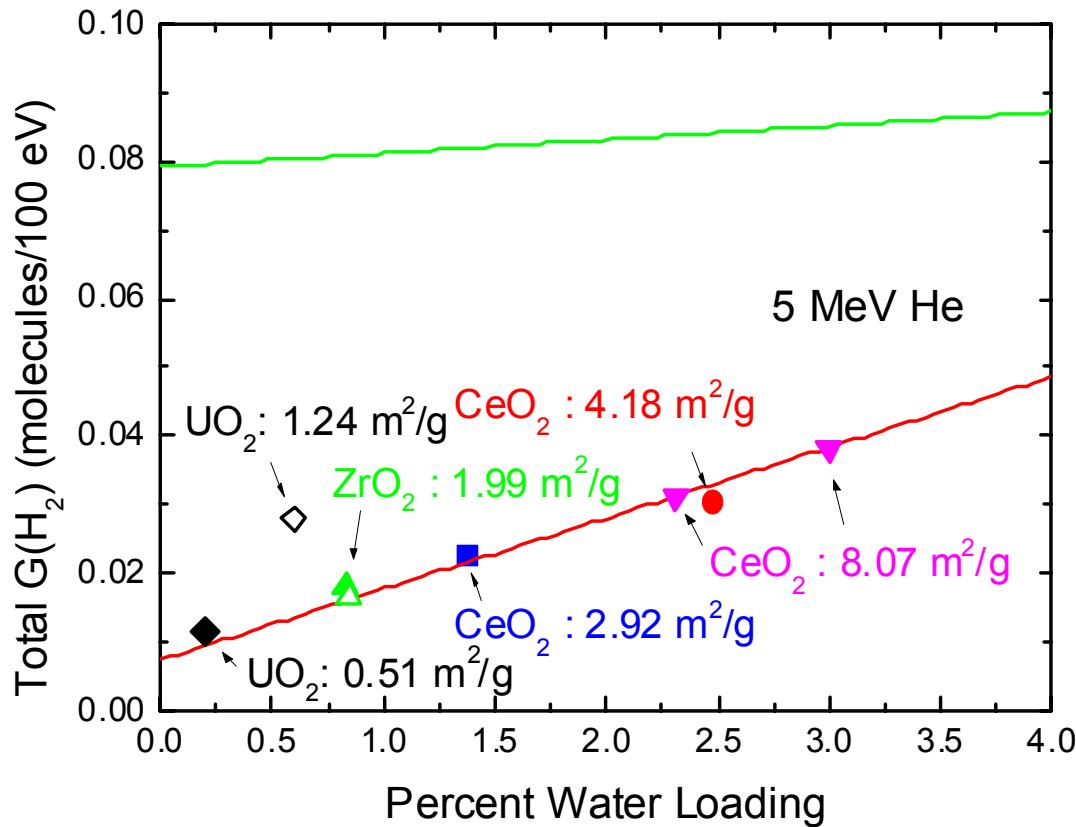
Yields determined with respect to water and oxide



ZrO₂ gives higher H₂ yield than other oxides.
H₂ yields dependent on water loading, except maybe UO₂.

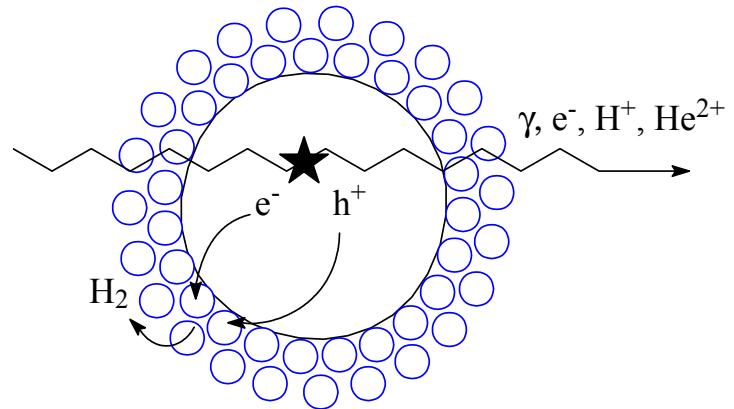
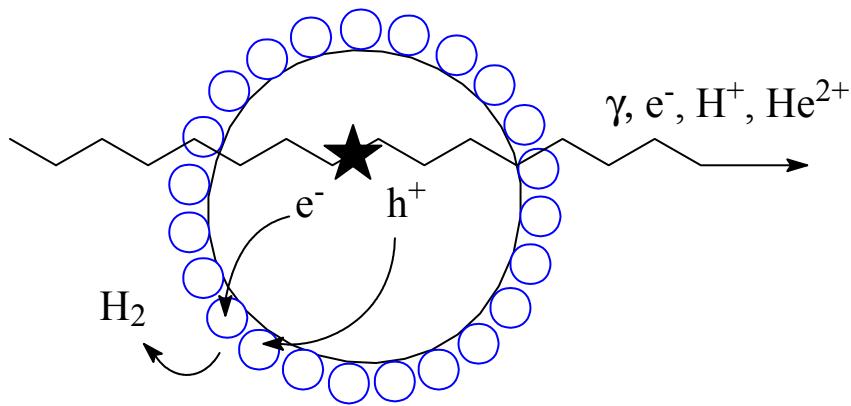
Total G-values for H₂ Production in α -Radiolysis

Yields determined with respect to total water



H₂ yields independent of oxide type, except maybe UO₂.

H_2 Dependence on Water Loading

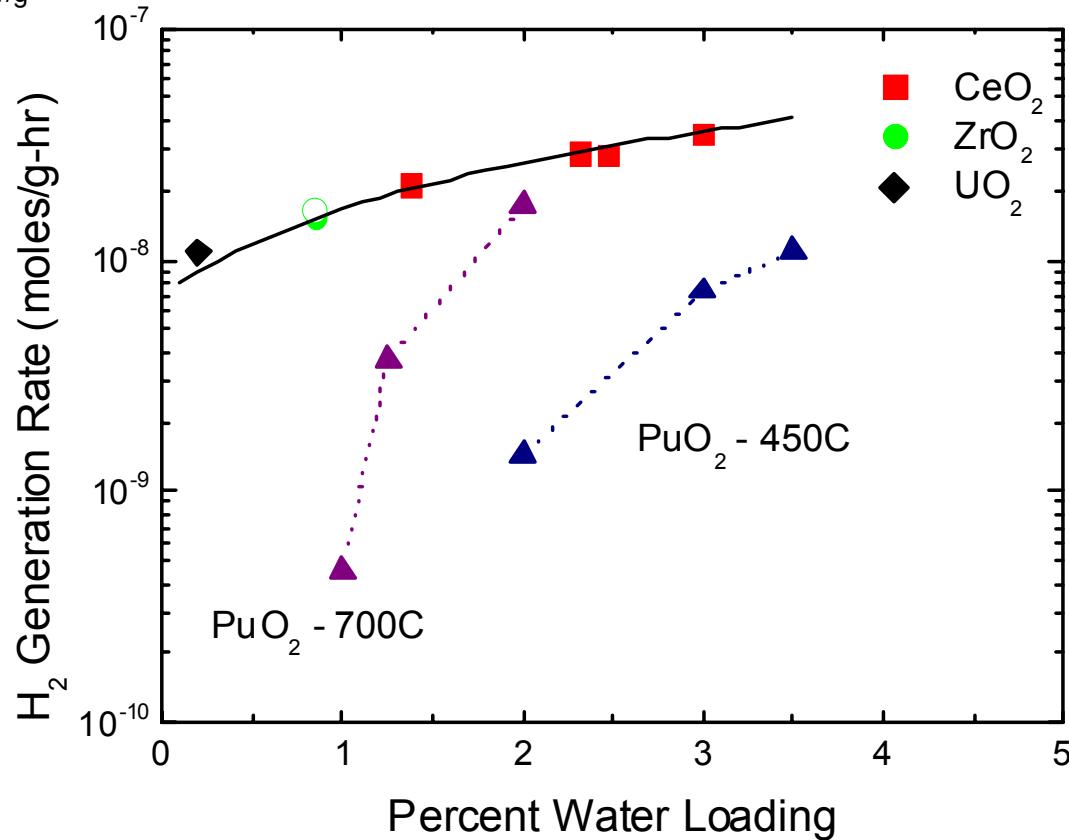


“Energy” from interior of oxide is able to induce chemistry in water.
Most of the chemistry probably occurs at the water/solid interface.
 O_2 suppresses H_2 yields by order of magnitude in ZrO_2 .
Particle size dependent studies should clarify “energy” carrier.

Comparison of H₂ Yields with PuO₂

PuO₂: R. R. Livingston and J. M. Duffey WSRC-TR-2001-00420

Assume 0.0025 W/g



Must compare data under similar conditions.
H₂ production sensitive to atmosphere.

Future Oxide Studies

Measure absolute yields of gaseous products in selected systems for application to waste storage.

Obtain fundamental mechanistic information to use in models.

Examine: H_2 (O_2) formation

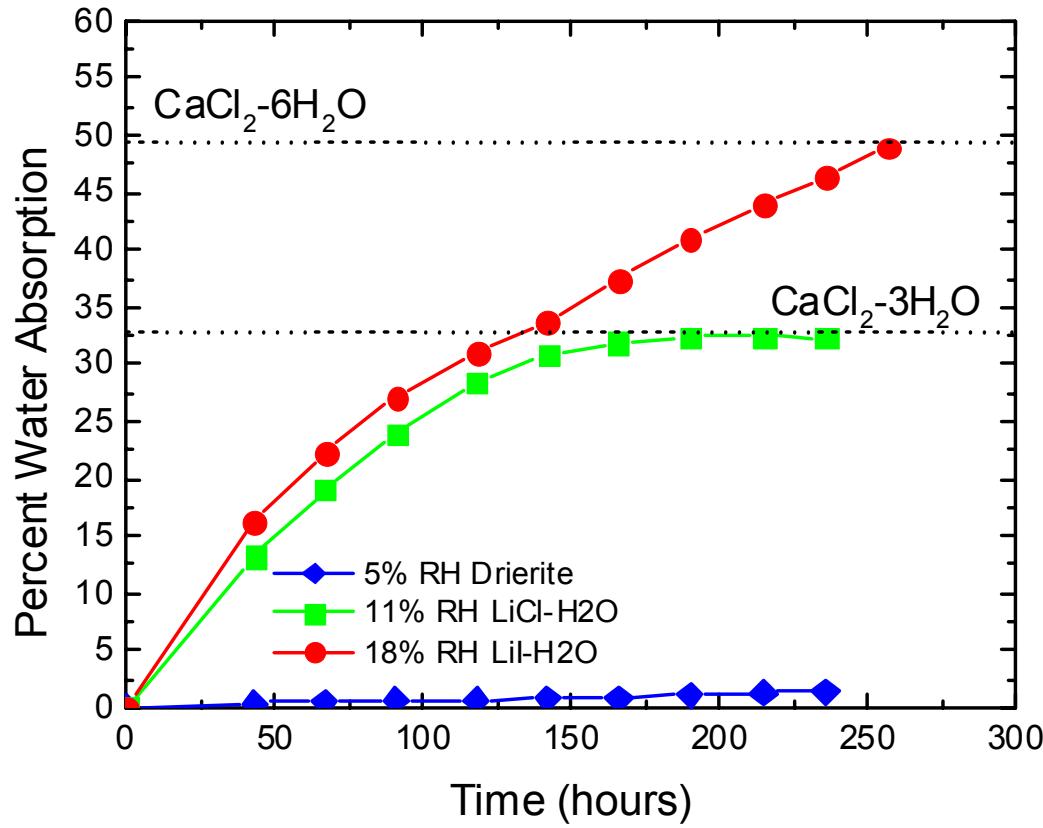
Atmospheric effects: Air, O_2 , inert (He, Ar)

Radiation: γ -rays and 5 MeV ${}^4\text{He}$ ions

Size Effects: ZrO_2 and CeO_2 of various sizes

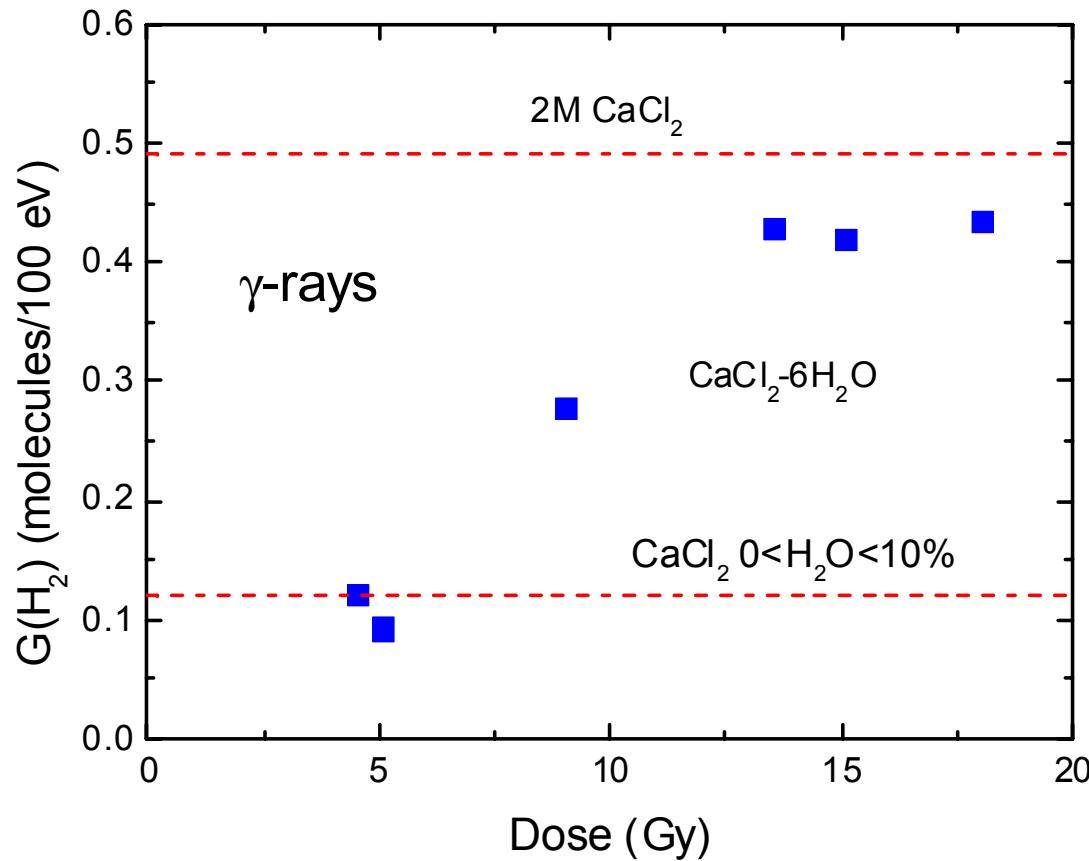
Different oxides: UO_2 , Pr_2O_3 , etc.

Water Loading on CaCl_2



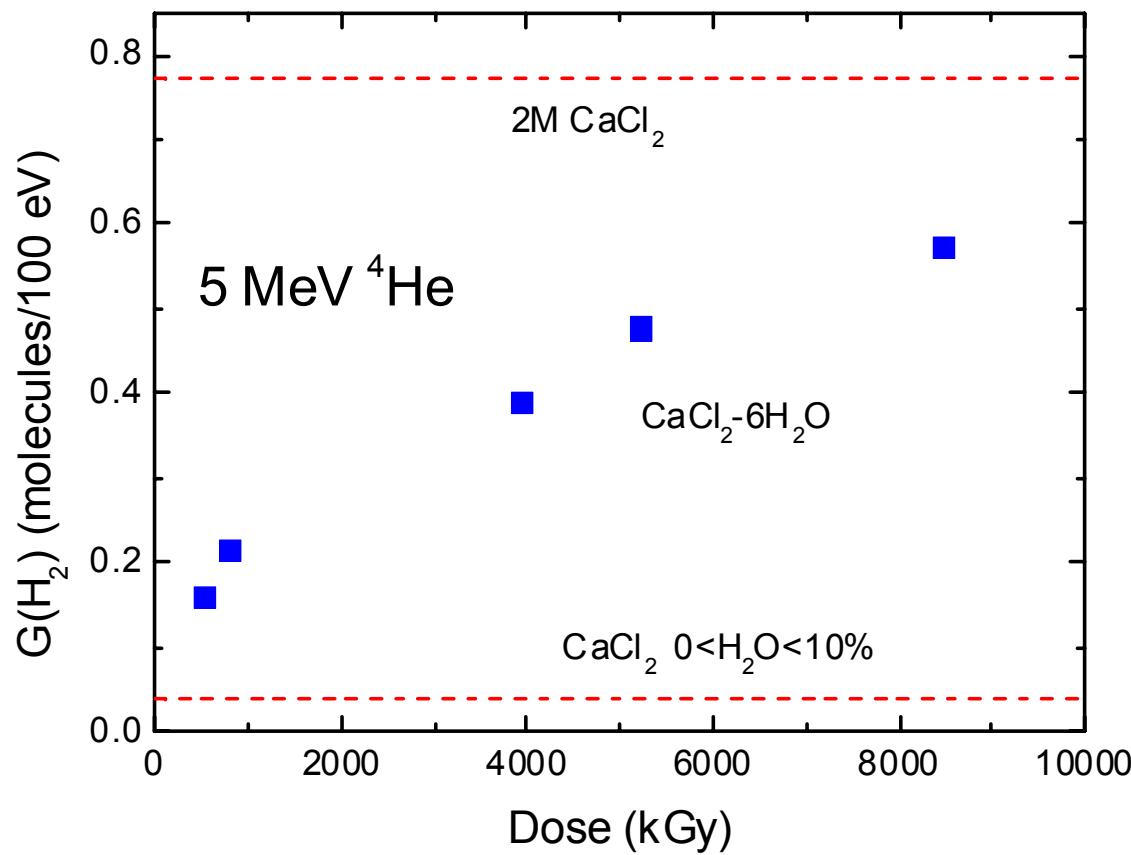
Rate of water loading depends on mass of salt,
equilibrium level does not.

H₂ Formation from γ -Radiolysis of CaCl₂



$G(H_2)=0.12$ for wet CaCl_2 ; $G(H_2)=0.49$ for 2M CaCl_2 .
 $G(H_2)$ for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ depends on “melting”, varies from value of wet CaCl_2 to that of solution.

H_2 Formation from α -Radiolysis of $CaCl_2$

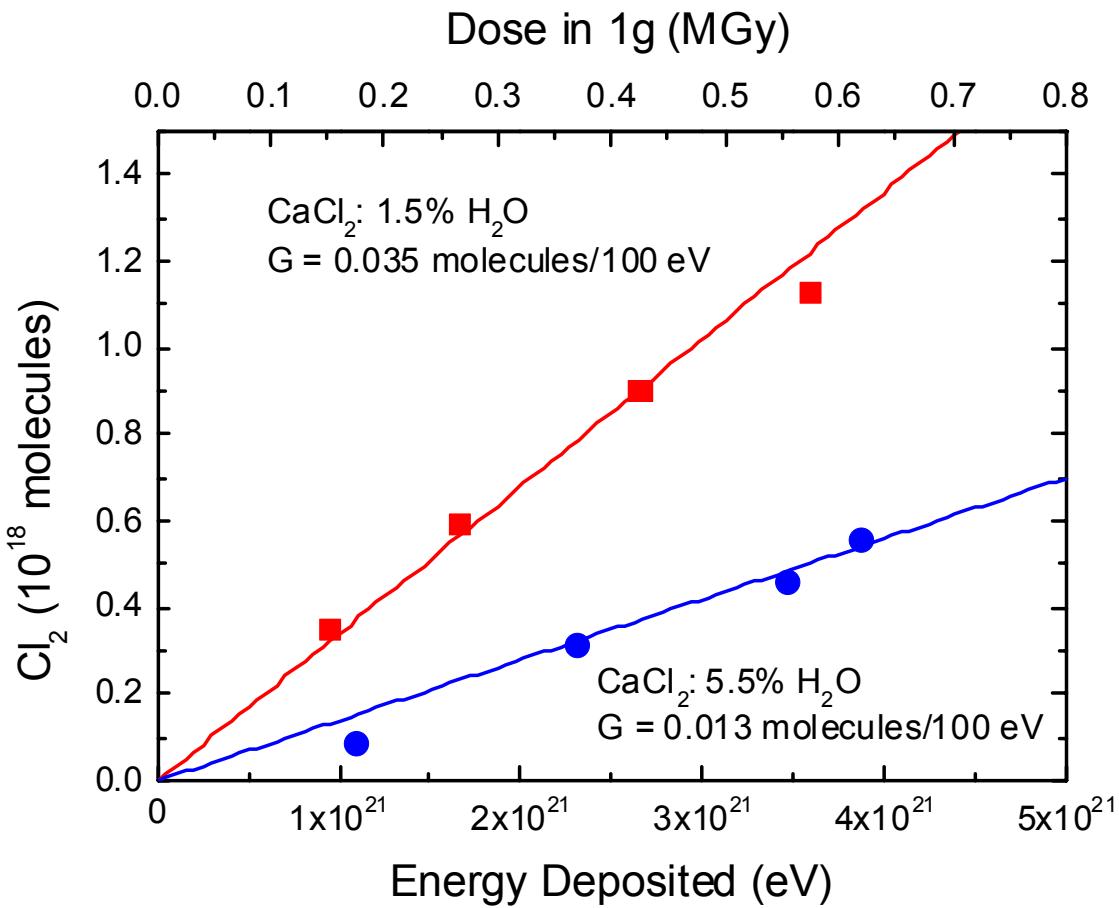


$G(H_2)=0.04$ for wet $CaCl_2$; $G(H_2)=0.77$ for 2M $CaCl_2$.

$G(H_2)$ for $CaCl_2 \cdot 6H_2O$ depends on “melting”.

Not a dose effect, but a heating effect due to radiolysis.

Cl_2 Formation from γ -Radiolysis of CaCl_2



Cl_2 yields low and very dependent on water loading:
No water – no Cl_2 ; > 10% water – no Cl_2 .

Future Salt Studies

Examine gas production from salts for application to pressure/explosion effects in waste storage containers.

Identify and quantify corrosive products.

Examine: H_2 and Cl_2 yields, color center formation

Radiation: γ -rays and 5 MeV ${}^4\text{He}$ ions

Salts: NaCl , KCl , MgCl_2

Mixtures: oxides - salts

Progress

Publications:

J. A. LaVerne and L. Tandon, H₂ Production in the Radiolysis of Water on CeO₂ and ZrO₂, *J. Phys. Chem. B.* **2002**, *106*, 380.

J. A. LaVerne and L. Tandon, H₂ Production in the Radiolysis of Water on UO₂, *in preparation*.

J. A. LaVerne and L. Tandon, Radiolysis of Water on CaCl₂, *in preparation*.